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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

- (54) Low-Lead Zinc Alloy Powders for Zero-Mercury Alkaline Batteries
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- (57) 3 Claims

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Notice: The specification contained herein as filed

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Abstract of the Disclosure

A mercury-free zinc alloy powder having a low gassing rate in the presence of iron up to 30 ppm, and consisting of 0.001 to 0.1 wt % lead, 0.01 to 0.1 wt % bismuth, 0.01 to 0.1 wt % indium and 0.01 wt % to 0.1 wt % Al, the balance being Zn and unavoidable impurities.

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LOW-LEAD ZINC ALLOY POWDERS FOR ZERO-MERCURY ALKALINE BATTERIES

This invention relates to low-lead zinc alloy powders for zero-mercury alkaline batteries displaying low and iron resistant after discharge gassing, hereinafter simply called gassing.

Background of the Invention

The role of mercury in suppressing gassing (due to hydrogen evolution) of zinc powders in alkaline battery electrolytes is well known. However, mercury is toxic and it has become highly desirable to provide mercury-free alkaline batteries.

Addition of alloying elements to zinc, namely bismuth, indium, gallium, aluminum, and other elements is known to reduce corrosion of mercury-free alkaline batteries, such as disclosed in U.S. patent No. 5,082,622. However, as disclosed in U.S. patent No. 5,108,494, gassing of mercury-free alkaline batteries made of zinc alloy powders is strongly dependent upon the iron content

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of the zinc power. According to the above patent, the iron content of the zinc powder used for making mercuryfree alkaline batteries must be kept below 1 ppm.

It is the object of the invention to provide zinc alloy powders for mercury-free alkaline batteries which display low gassing even in the presence of higher amounts of iron.

Summary of the Invention

The present invention provides mercury-free (also called non-amalgamated) zinc alloy powders which are characterized by a low gassing rate in the presence of iron up to 30 ppm. The zinc alloy powder in accordance with the present invention consists of 0.001 to 0.1 wt % lead, 0.01 to 0.1 wt % bismuth, 0.01 to 0.1 wt % indium and 0.01 to 0.1 wt % Al, the balance being zinc and unavoidable impurities.

The bismuth or indium content of the zinc alloy powder is preferably from 0.05 to 0.1 wt % so as to produce a zinc alloy powder exhibiting negligible sensitivity to iron concentration up to 30 ppm.

Short Description of the Drawing

The invention will now be disclosed, by way of example, with reference to specific examples and to the accompanying drawing which illustrates the iron effect on gassing for various zinc alloy powders.

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Detailed Description of the Invention

Preliminary tests have shown that the addition of bismuth, or indium to a zinc alloy containing 500 ppm of lead and less than 5 ppm iron increases gassing, while the combination of bismuth and indium is not efficient in reducing gassing. Only aluminum was found to reduce gassing. The above is shown in the following table.

TABLE I

	Nomin	Gassing		
10	Bi .	In	A1	microl/g-day
	0	. 0	0	44
	0	0	300	· 45
•	0	500	0	264
	0	500	300	60
15	500	0	0	144
	500	0	300	59
	500	500	0	208
Ç. V	500	500	300	18

It also has been found that a reduction in impurity content such as antimony, is not sufficient to

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suppress gassing of regular lead-zinc alloys (lead at 500 ppm), unless iron is also reduced to the lowest level (1 ppm). Indeed, a linear relationship was found between gassing of regular lead-zinc alloys and the corresponding iron content. The sensitivity was found to be 20 microl/g-day per ppm.

Applicant has surprisingly found, in accordance with the present invention, that the problem of sensitivity of zinc powder towards iron contamination can be solved by adding to a low-lead zinc powder specific combinations of Bi, In and Al.

The following describes the embodiments of the present invention. The requisite alloys were prepared by addition of the respective alloying elements in their metallic form to molten zinc. The molten alloys were converted to powder using low-pressure, dry-air atomizing. The obtained product was not sieved.

Examples 1 to 4

Zinc containing 250 ppm lead was alloyed with bismuth, indium and aluminium. The starting material was zinc ingot having an iron content around 2 ppm. Iron was successively added by dissolving steel in molten zinc.

As shown in Table 2, Bi-In-Al zinc alloys containing 250 ppm lead and more than 200 ppm of indium or/and bismuth display a strong resistance to iron contamination. In comparison, a lead (250 ppm) - zinc

powder containing less than 5 ppm iron exhibits a gassing rate of 130 microl/g-day.

TABLE 2

	P	Gassing			
Lead	Bismuth	Indium	Aluminium	Iron	
(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	microl/g-day
250	200	200	600	3	46
				13	67
	·			26	153
250	500	200	300	5	33
				7	41
				11	66
250	200	500	300	2	34
,				9	20
				20	40
250	500	500	600	4	33
				8	28
				18	37

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Examples 5 to 8

Zinc containing less than 25 ppm of lead was alloyed with bismuth, indium and aluminium. The starting material was zinc ingot having an iron content lower than 2 ppm. Iron was successively added by dissolving steel in molten zinc.

As shown in Table 3, Bi-In-Al zinc alloys containing less than 25 ppm lead and more than 200 ppm of Indium or/and Bismuth display a strong resistance to iron contamination. In comparison, the gassing of zinc powder containing no alloying element and less than 5 ppm of iron is around 400 microl/g-day.

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TABLE 3

	Gassing				
Lead	Bismuth	Indium	Aluminium	Iron	
(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	microl/g-day
< 25	200	200	300	5	42
				17	93 .
				29	249
< 25	500	200	600	6	64
				6	68
			. <i>.</i>	12	66
< 25	200	500	600	3	72
				10	50
				19	78
< 25	500	500	300	4	63
	,			13	35
	·			24	70

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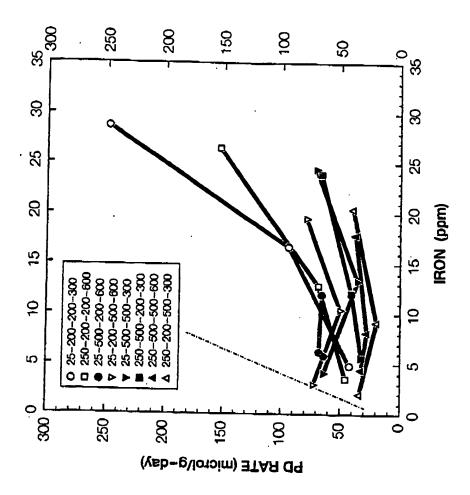
A graph showing the effect of iron composition in zinc alloys powder on the gassing rate is shown in the accompanying drawing. All the alloys described in example 1 to 8 above are plotted. The dependence of regular lead zinc powder on iron contamination is also shown by a dashed line.

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CLAIMS

- 1. A mercury-free zinc alloy powder having a low gassing rate in the presence of iron up to 30 ppm, consisting of 0.001 to 0.1 wt % lead, 0.01 to 0.1 wt % bismuth, 0.01 to 0.1 wt % indium and 0.01 wt % to 0.1 wt % Al, the balance being Zn and unavoidable impurities.
- 2. A mercury-free zinc alloy powder as defined in claim 1, containing 0.05 to 0.1 wt % bismuth, exibiting a negligible sensitivity to iron concentration up to 30 ppm.
- 3. A mercury-free zinc alloy powder as defined in claim 1, containing 0.05 to 0.1 wt % indium, exibiting a negligible sensitivity to iron concentration up to 30 ppm.



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